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DETERMINATION OF MANGANESE IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS WITH PAN

by

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SUMMARY

A spectrophotometric method for determining 0.0005 - 0.10% of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and separation of the matrix materials by extraction of their cupferrates, the red complex formed between manganese^{II} and PAN [1-(2-pyridylazo)-2-naphthol] is extracted into chloroform from an ammoniacal tartrate-cyanide medium. The absorbance of the resulting extract is determined at 562 mμ. With the exception of zinc and lead, other impurities present in the four high-purity metals described do not interfere in the proposed method.

INTRODUCTION

The determination of impurities in high-purity niobium, tantalum, molybdenum and tungsten metals is a continuing analytical project of the Mines Branch laboratories concerning the properties of refractory metals. As part of this project, the present investigation was undertaken to develop a spectrophotometric procedure for determining trace amounts of manganese that would be applicable to all four metals.

Published information pertaining to the determination of small amounts of manganese in matrices of the above metals is meagre. Several

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spectrophotometric procedures have been applied to the determination of manganese in niobium[1], molybdenum[2] and tungsten[3] metals, but none of these methods is directly applicable to all four metals under consideration.

The most widely used method for determining manganese spectrophotometrically is based on the oxidation of manganous to permanganate ion with a suitable oxidizing agent. Because of its low sensitivity this method was not considered in the present investigation. Recently, methods[4-11] of considerably greater sensitivity than the permanganate method have been proposed for the determination of small amounts of manganese. Methods involving PAN [1-(2-pyridylazo)-2-naphthol] as the chromogenic reagent have been reported in which the molar absorptivities for the manganese^{II}- PAN complex in chloroform[4] and in ether[5,6] have been found to be 4×10^4 and 5.85×10^4 at 550 and 560 mμ respectively. Because of the high sensitivity inherent in the use of PAN it was decided to investigate its possible application in the present work.

This paper describes a procedure for determining manganese spectrophotometrically in high-purity niobium, tantalum, molybdenum and tungsten metals with PAN after the matrix materials have been removed by extraction of their cupferrates. The procedure used for dissolution of the samples is essentially that previously reported in methods for determining iron[12], copper[13] and nickel[14]. Zinc and lead interfere in this method, but quantities up to 50 and 100 μg, respectively, can be tolerated in the aliquot taken for analysis without causing appreciable error in the manganese determination.

EXPERIMENTAL

Apparatus

Spectrophotometer: Unicam Model SP 500

pH meter: Leeds and Northrup

Centrifuge: Canlab clinical type

Teflon (tetrafluoroethylene) beakers: 250 and 400 ml; Dynalab Corp., Rochester, N.Y., U.S.A.

Separatory funnels (Nalgene): 500 ml pear shape type; The Nalge Co., Inc., Rochester, N.Y., U.S.A.

Reagents

Water: De-ionize by passing distilled water through a column of Dowex 50W-X8 resin.

Standard manganese solution: Dissolve 0.1000 g of electrolytic manganese in 10 ml of 1:1 sulphuric acid and dilute to 500 ml with water. Dilute 5 ml of this stock solution to 500 ml with water. Prepare fresh as needed (1 ml of this diluted solution = 2 µg of manganese).

PAN, 0.1% solution: Dissolve 0.100 g of 1-(2-pyridylazo)-2-naphthol (J.T. Baker Chemical Co.) in ethyl alcohol and dilute to 100 ml with ethyl alcohol.

Ammonium tartrate, 10% solution: Dissolve 20 g of ammonium tartrate in water and dilute to 200 ml.

Hydroxylamine hydrochloride, 20% solution: Dissolve 20 g of hydroxylamine hydrochloride in water and dilute to 100 ml. Prepare a fresh solution daily.

Buffer solution: Dissolve 10 g of ammonium chloride in water and add 100 ml of concentrated ammonia solution (approximately 58% ammonium hydroxide). Dissolve 1.200 g of potassium cyanide in this solution, dilute to 200 ml with water and store in a polyethylene bottle.

Cupferron, 9% solution: Prepare a fresh solution as required.

Chloroform: Analytical reagent, obtained from Mallinckrodt Chemical Works.

Isoamyl alcohol: Analytical reagent, obtained from Fisher Scientific Company.

Colour Development and Preparation of Calibration Curve

Add 1 ml of 10% ammonium tartrate solution to each of seven 60-ml separatory funnels that are marked at 25 ml; then, by burette, add to the last six funnels 1, 2, 3, 4, 5 and 6 ml, respectively, of standard manganese solution (i.e. 1 ml = 2μg of manganese). (The stem of each funnel is first rinsed with ethyl alcohol to remove water droplets). The first funnel contains the blank. Add to each funnel 5 ml of 20% hydroxylamine hydrochloride solution, dilute to the 25-ml mark with water, stopper and mix. (Because chloroform is soluble to a certain extent in water, i.e., 10 g/l at 15°, the total volume should be kept relatively constant.) Then, working with one solution at a time, add 5 ml of buffer solution and 3 ml of 0.1% PAN solution, and mix well after each addition. Allow exactly 45 seconds to elapse (timed from the start of the addition of PAN solution), then add, by pipette, 10 ml of chloroform, stopper and shake for 2 minutes.

Allow 3 minutes for the layers to separate, then drain the chloroform extract into a 15-ml centrifuge tube and centrifuge for 30 seconds. (If the aqueous phase remains too long in contact with the organic phase low results will be obtained.) Determine the absorbance of each extract against the blank as the reference solution, using 1-cm cells, at a wavelength of 562 mμ. Plot μg of manganese vs absorbance.

Procedure

In the following procedures a reagent blank is carried along with the samples.

1) Niobium and Tantalum Metals: Transfer a 0.5000 g sample of the powdered metal to a 250-ml Teflon beaker, add 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon cover. Through the lip of the beaker add concentrated nitric acid slowly, approximately 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. Add 3 ml of formic acid to destroy excess nitric acid and heat gently until the evolution of brown oxides of nitrogen ceases. Wash down the sides of the beaker with a minimum amount of water, evaporate to approximately 5 ml and add 1 ml of hydrofluoric acid and 20 ml of 1:1 sulphuric acid. (If the solution remains slightly cloudy at this stage, warm gently until it clears.) Wash down the sides of the beaker with 1:1 hydrochloric acid and transfer the resulting solution to a 500-ml Nalgene separatory funnel.

Dilute to approximately 100 ml with water, stopper, mix and cool on ice for about one hour. Then, add 100 ml of cold, freshly prepared 9% cupferron solution, mix, add 50 ml of cold chloroform and shake for 1 minute. Allow 5 minutes for the layers to separate, then drain off and discard the organic layer. Repeat the extraction with 20 ml of cupferron solution and 25 ml of chloroform, and, finally, with four successive 10-ml portions of chloroform. Transfer the aqueous phase to a 400-ml Teflon beaker, cover, heat gently to remove excess chloroform, then evaporate the solution to fumes of sulphur trioxide with the addition of 20 ml each of concentrated nitric and hydrochloric acids to destroy residual organic material. Cool, wash down the sides of the beaker with water, evaporate to fumes again, and repeat to ensure complete removal of hydrofluoric acid. Dilute the solution with approximately 10 ml of water, wash down the sides of the beaker with 1:1 hydrochloric acid, transfer to a 250-ml pyrex beaker and evaporate to dryness. Again, wash down the sides of the beaker with 1:1 hydrochloric acid and evaporate to dryness. Add 5 ml of 10% ammonium tartrate solution and 20 ml of water to the residue in the beaker and heat gently until the solution is clear. Then add 1 ml of hydrochloric acid and dilute to approximately 35 ml with water. Using a pH meter, adjust the pH of the resulting solution to 3.5 $\pm$0.2 with concentrated ammonia solution, transfer to a 100-ml volumetric flask and dilute to volume. Transfer a suitable aliquot (2 - 20 ml) of both sample and blank solutions, depending on the manganese content of the sample, to 60-ml separatory funnels and analyze the solution for manganese by the

procedure given under "Calibration Curve". When 20-ml aliquots of sample solution are taken:

1 µg of manganese = 0.001%

2) Molybdenum Metal: Decompose a 0.5000 g sample of the powdered metal in a 250-ml pyrex beaker with 20 ml of 1:1 sulphuric acid and 2 ml each of concentrated nitric and hydrochloric acids. Evaporate the resulting solution to fumes of sulphur trioxide, cool, wash down the sides of the beaker with water, and again evaporate to fumes to ensure complete removal of nitric acid. Proceed with the cupferron-chloroform extraction of molybdenum and the subsequent determination of manganese as described above for niobium and tantalum metals, using glass funnels and beakers and omitting the procedure for the removal of hydrofluoric acid.

3) Tungsten Metal: Decompose a 0.5000 g sample of the powdered metal as described above for niobium and tantalum metals. After removal of excess nitric acid with formic acid, add 1 ml of hydrofluoric acid and 70 ml of 1:1 sulphuric acid. Then proceed with the extraction of tungsten cupferrate as described above, using in succession 100, 50, 25, 15, 15 and 15 ml of a 2:1 mixture of chloroform and isoamyl alcohol as extractant instead of chloroform. Gently evaporate the aqueous phase until approximately 150 ml remain. (The solution will be black at this stage because of the large quantity of organic material present.) Cool on ice, add 20 ml each of nitric and hydrochloric acids and let stand at room

temperature until most of the organic material has decomposed. Then proceed with the determination of manganese according to the method described for niobium and tantalum metals.

RESULTS

Extraction of the Coloured Complex

Shibata[5,6] showed that the manganese^{II}-PAN complex can be extracted into various organic solvents, but stated that it is extracted most efficiently with ether or chloroform. Tests carried out in this laboratory with n-amyl alcohol, chloroform, benzene and carbon tetrachloride yielded considerable differences in the absorption maximum of the complex in these solvents, i.e., 558, 562, 568 and 570 mμ, respectively. Ether was not included in these tests because Shibata[5] had already shown that the absorption maximum of the complex in ether occurs at 560 mμ. The results of these tests showed that chloroform and benzene are equally efficient extractants and also indicated that the molar absorptivity of the complex varies considerably with the solvent employed. The molar absorptivities in ether, chloroform and benzene were 5.85×10^4[5], 4.8×10^4 and 4.7×10^4, respectively. Although the molar absorptivity of the complex is greatest in ether, chloroform was chosen for the present investigation because it is less noxious than ether or benzene.

Preliminary experiments carried out at pH 9 with test solutions containing ammonium chloride, hydroxylamine hydrochloride and potassium cyanide showed that up to at least 12 μg of manganese contained in approximately 25 ml of solution can be extracted quantitatively in a

single stage with 10 ml of chloroform. The extraction of larger amounts was not attempted because of the high absorbance of the resulting extract. The absorbance of the chloroform extract of the manganese^{II}-PAN complex remains constant for hours after extraction and only decreases slightly if allowed to stand for 24 hours.

Factors Influencing the Formation and Subsequent Extraction of the Manganese^{II}-PAN Complex

Effect of Reductant: Erratic results were obtained in preliminary experiments carried out at approximately pH 9 when the PAN reagent was added to ammoniacal test solutions containing ammonium chloride and potassium cyanide (to complex copper and other impurities present in the water and reagents used). It was considered that this effect could be caused by partial air-oxidation of the manganese, because previous investigators[15,16] have shown that atmospheric oxidation of manganese^{II} to manganese^{III} takes place in alkaline media. Oelschläger[17] and Stary[18] state that this effect can be prevented by the addition of hydroxylamine hydrochloride, and subsequent tests performed in the presence of an excess of this reducing agent yielded consistent and reproducible results.

Effect of pH: Previous investigators have not defined clearly the optimum pH range for the complete formation of the manganese^{II}- PAN complex. The results obtained by Shibata[5], Betteridge et al[19] and Berger and Elvers[4] indicate pH ranges of approximately 9 to 11, 8.5 to 9.6 and 8 to 10, respectively. To define this range more precisely, pH experiments were carried out on test solutions containing 10 µg of manganese, using 5 ml

each of a series of buffer solutions of increasing pH (prepared by dissolving 5 g of ammonium chloride and 100 mg of potassium cyanide in water, adding varying quantities of concentrated ammonia solution and diluting to 100 ml). The pH at which the complex was formed in these test solutions was determined by measuring the pH of the aqueous phase after the complex was extracted. The results of these tests showed that, for the pH range tested (approximately 6 to 10), the manganese^{II}-PAN complex is completely formed and extracted in a single stage with 10 ml of chloroform in the pH range 8.8 to 9.6

On the basis of these results, an intermediate pH of 9.2 was chosen for the present work. This pH was obtained in the above tests with a buffer solution containing 50 ml of concentrated ammonia solution in a volume of 100 ml.

Effect of PAN Concentration: Shibata[6] states that 1 ml of 0.1% PAN solution suffices to complex 10 μg of manganese, but this amount was not sufficient under the conditions of the present investigation, in which the PAN solution was added after the buffer solution. This order of addition of reagents was chosen to complex copper and other impurities present in the water and reagents used with potassium cyanide at pH 9.2 prior to formation of the manganese^{II}-PAN complex. Tests performed with varying amounts of PAN solution showed that at least 3 ml of 0.1% PAN solution are required to complex 10 μg of manganese under the above conditions.

Effect of Potassium Cyanide and Ammonium Tartrate: Although PAN is known to form extractable complexes with a great number of

metallic ions[20], previous investigators of PAN reactions have shown that cyanide and citrate are effective complexing agents for many of these metals[20,6]. Therefore, tests were undertaken to determine the maximum amounts of these complexing agents that could be present during extraction of the manganese^{II}-PAN complex without appreciably affecting the manganese result. The effect of potassium cyanide alone was first tested on solutions containing 10 µg of manganese, using a series of buffer solutions of varying potassium cyanide content (otherwise prepared as described under "Reagents"). The results of these tests showed that up to 30 mg of potassium cyanide can be present during extraction without affecting the determination of manganese.

Preliminary tests carried out with ammonium citrate yielded low results for manganese. However, similar tests with ammonium tartrate indicated that its inhibiting effect on the manganese-PAN reaction is considerably less than that of citrate. This result is corroborated by Jones[21] who showed that, during extraction of the manganese diethyldithiocarbamate complex with chloroform, the competitive complexing action of citrate is much greater than that of tartrate.

The effect of varying amounts of ammonium tartrate was tested on solutions containing the maximum tolerable amount of potassium cyanide (i.e. 30 mg) found previously. The results of these tests showed that, although ammonium tartrate interferes slightly, up to 100 mg can be present in the solution taken for extraction without causing excessive error in the manganese result.

Effect of Time: Although the results obtained by Shibata[6] indicate that the manganese^{II}-PAN complex remains stable in solution (presumably prior to extraction) over a time interval of 2 to 60 min., this is not true in the present investigation under the competitive complexing influence of cyanide and tartrate ions. The results (Table I) of tests carried out in media containing cyanide alone and cyanide plus tartrate, in which the time interval from the beginning of the addition of PAN solution to the start of the chloroform addition was varied from 30 sec. to 30 min., show the effect of time on the stability of the manganese complex. The results also show that the rate of dissociation of the complex is dependent on the concentration of cyanide and tartrate ions present in solution. Relatively consistent results were obtained for the 30 and 45 sec. time intervals; consequently the latter was chosen for the present work mainly for convenience.

Table I - Effect of Time on the Stability of the Manganese^{II} - PAN Complex

	Absorbance	
	I	II
Time	Potassium cyanide taken, 5 mg	Potassium cyanide taken, 30 mg
30 sec.	0.874	0.868
45 "	---	0.873
1 min.	0.879	0.854
2 "	0.847	0.787
3 "	0.834	0.750
5 "	0.813	0.750
15 "	0.781	0.655
30 "	0.781	0.597
	III	IV
	Potassium cyanide taken, 5 mg. Ammonium tartrate taken, 100 mg	Potassium cyanide taken, 30 mg. Ammonium tartrate taken, 100 mg
30 sec.	0.852	0.868
45 "	---	0.867
1 min.	0.867	0.853
2 "	0.824	0.758
3 "	0.807	0.731
5 "	0.787	0.685
15 "	0.752	0.621
30 "	0.765	0.562

Manganese taken, 10 µg.

Separation of Niobium, Tantalum, Molybdenum and Tungsten by Extraction of their Cupferrates

Preliminary experiments to determine the applicability of the manganese-PAN-chloroform extraction procedure to the determination of manganese in solutions of the four high-purity metals were carried out on a synthetic sample of each metal decomposed according to the procedure described for niobium and tantalum metals. In these tests, boric acid and ammonium tartrate were utilized to complex excess hydrofluoric acid and the matrix elements, respectively. The results of these tests showed that incomplete recovery of the added manganese was obtained from all four solutions. Further investigation showed that this was caused by the presence of boric acid and also by the excessive amount of ammonium tartrate required to complex the matrix elements. (Although boric acid alone does not interfere in the manganese determination, low results are obtained if both boric acid and ammonium tartrate are present in the solution taken for extraction). Consequently, it was considered that the separation of the matrix materials from the manganese might provide a more effective means of determining manganese in the four metals under consideration. Other investigators[22, 23] have shown that the cupferrates of niobium, tantalum and molybdenum can be extracted with chloroform from a strong sulphuric acid medium; consequently, this separation technique was utilized in the present investigation.

Tungsten is precipitated by cupferron from strong acid solution[22] but its cupferrate is relatively insoluble in chloroform. Allen and

Hamilton[24] investigated the partition of small amounts of tungsten cupferrate (20 μg of tungsten) between aqueous solutions and a series of immiscible organic solvents and showed that it is most efficiently extracted with isoamyl alcohol. They also studied the effect of sulphuric acid concentration on the extraction with isoamyl alcohol and concluded that a concentration of 6 N is satisfactory for 98 - 100% extraction of tungsten when four extractions are performed. The applicability of their procedure to the separation of large amounts of tungsten was investigated in the present work.

Experiments were performed with tungsten solutions prepared by decomposing 0.5000 g of tungsten metal according to the procedure described for niobium and tantalum metals. A 2:1 mixture of chloroform and isoamyl alcohol was employed as extractant in these tests. The results of these tests showed that large amounts of tungsten cupferrate can be extracted by the above solvent mixture, but because of the large volume of cupferron solution required to complex 0.5000 g of tungsten, the initial concentration of sulphuric acid has to be increased to approximately 12 N prior to the addition of cupferron solution. Under these conditions chemical analysis showed that between 14 and 21 mg of tungsten remained in the aqueous phase after extraction and this amount does not interfere in the determination of manganese.

Effect of Diverse Ions

Previous investigators[4-6, 20] have shown that the following ions also form coloured metal complexes with PAN: bismuth^{III}, cadmium^{II},

copper^{II}, palladium^{II}, platinum, tin^{IV}, uranium (UO_2^{II}), mercury^{II}, thorium^{II}, cobalt^{II}, lead^{II}, iron^{II}, iron^{III}, nickel^{II}, zinc^{II}, lanthanum^{III}, cerium^{III}, cerium^{IV}, indium^{II}, indium^{III}, scandium^{III}, europium^{II}, gallium^{III}, yttrium^{III}, vanadium^{V} and gold. These authors investigated qualitatively the effect of various complexing agents (i.e. ethylenediaminetetraaceticacid, cyanide, fluoride and citrate) on the formation of some of the above PAN complexes. Because the formation and stability of PAN complexes and also the effectiveness of cyanide as a complexing agent are greatly influenced by pH, it was considered expedient to investigate the possible interference effects of those of the above ions plus other ions that could occur as impurities in samples of the four high-purity metals.

The results of these tests showed that 1 mg each of nickel^{II}, copper^{II}, cadmium^{II}, phosphorus^{V}, chromium^{III}, vanadium^{V}, aluminum^{III}, zirconium^{IV}, iron^{III}, arsenic^{V}, antimony^{III}, antimony^{V}, tin^{IV}, titanium^{IV}, silicon^{IV} and bismuth^{III} (added in the valence states shown) do not interfere in the determination of manganese by the proposed method. However, 1-mg quantities of zinc^{II}, lead^{II} and cobalt^{II} do interfere. Zinc is ineffectively complexed with small amounts of cyanide under the described experimental conditions but forms a very stable, extractable PAN complex (formation constant $10^{21.8}$)[19]. Test solutions containing lead (or bismuth) turned a dark reddish-brown colour on addition of PAN but cleared up on shaking with chloroform. Low results were obtained with test solutions containing 1 mg of cobalt, even though the cobalt appeared to be completely complexed with cyanide. However, up to at least 50, 100 and 500 µg of zinc,

lead and cobalt, respectively, can be tolerated separately in the proposed method without causing an appreciable error in the m nganese result.

Application to Synthetic Niobium, Tantalum, Molybdenum and Tungsten Samples

To determine the accuracy of the proposed method, it was applied to the analysis of a series of synthetic samples in which the added manganese varied from 0.001 to 0.10%. The standard manganese solution was added directly to the powdered metal samples. The results obtained are given in Table II.

Table II - Recovery of Manganese by the Proposed Method from Synthetic Niobium, Tantalum, Molybdenum and Tungsten Samples

Sample	Total Mn Present, %	Mn Found, %	Sample	Total Mn Present, %	Mn Found, %
Nb + 0.0010% Mn	0.0011	0.0011	Ta + 0.0010% Mn	0.0010	0.0010
Nb + 0.0050% Mn	0.0051	0.0050	Ta + 0.0050% Mn	0.0050	0.0048
Nb + 0.0100% Mn	0.0101	0.0101	Ta + 0.0100% Mn	0.0100	0.0099
Nb + 0.0250% Mn	0.0251	0.0249	Ta + 0.0250% Mn	0.0250	0.0250
Nb + 0.0500% Mn	0.0501	0.0504	Ta + 0.0500% Mn	0.0500	0.0502
Nb + 0.1000% Mn	0.1001	0.0998	Ta + 0.1000% Mn	0.1000	0.1005
Mo + 0.0010% Mn	0.0013	0.0013	W + 0.0010% Mn	0.0010	0.0009
Mo + 0.0050% Mn	0.0053	0.0052	W + 0.0050% Mn	0.0050	0.0049
Mo + 0.0100% Mn	0.0103	0.0103	W + 0.0100% Mn	0.0100	0.0100
Mo + 0.0250% Mn	0.0253	0.0253	W + 0.0250% Mn	0.0250	0.0248
Mo + 0.0500% Mn	0.0503	0.0507	W + 0.0500% Mn	0.0500	0.0497
Mo + 0.1000% Mn	0.1003	0.1017	W + 0.1000% Mn	0.1000	0.0988

Duplicate determinations of manganese in the above Nb, Ta, Mo and W metals by the proposed method gave average results of 0.0001%, none detected, 0.0003% and none detected, respectively.

DISCUSSION

Table II shows that the results obtained by the proposed method agree favourably with the total calculated percentage of manganese in the range of values up to approximately 0.1%.

Although tests were performed to determine the possible interference effects of various impurities that could occur in samples of the four high-purity metals under consideration, some of these impurities (i.e. copper, vanadium, zirconium, iron, antimony, tin and titanium) are partially or completely removed in the proposed method by extraction of their cupferrates.

In preliminary tests carried out to determine the applicability of cupferron-chloroform extraction to the separation of niobium, tantalum and molybdenum from small amounts of manganese, slightly low results were obtained for the added manganese. This error was found to be caused by partial oxidation of manganese to manganese dioxide during evaporation to dryness of the aqueous phase remaining after the extraction. However, this problem was avoided by dissolving the manganese dioxide adhering to the sides of the beaker with hydrochloric acid.

The pH range required for quantitative extraction of the manganese^{II}-PAN complex in a single stage with 10 ml of chloroform is approximately 8.8 to 9.6, but complete extraction can also be obtained at higher pH (approximately 10) by performing three extractions. However, because of the solubility of PAN in chloroform and the instability of the manganese complex in ammoniacal tartrate-cyanide media, additional PAN

solution must be added prior to each extraction step in order to recomplex the residual manganese resulting from the dissociation of its PAN complex. The combined extracts may then be diluted to a definite volume with chloroform prior to spectrophotometric measurement. Low results are obtained if ethyl alcohol is used as diluent.

The method presented in this paper is suitable for samples containing 0.0005 - 0.10% of manganese, but manganese contents below 0.0005% can be determined fairly accurately because the reagent blank contains approximately 0.5 µg or less of manganese. The method is extremely sensitive, the technique required is simple, and results are reproducible under routine conditions.

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